CLAY PIGMENTS AS INDICATORS OF PAINT AUTHENTICITY AND MATERIAL PROVENANCE

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Artist's pigments identified in colour layers of paintings are traditionally considered to be relevant for approximate dating based on literary evidence of exploitation, industrial production and use of different types of pigments in the history. Problems appear in older paintings, where written references are poor or missing and where, on the other hand, just the pigment presence is the only reliable evidence of its preparation and using in the fine art. This inconvenience together with difficulties caused by small size and heterogeneity of painting fragments, imprecise and frequently even incorrect interpretations of mineral assemblages in colour layers, caused that artistic styles are the only widely accepted headings of painting authenticity. Materials and technical features are underestimated—they are objective, but difficult to obtain and compare, especially because fragments with size less than 1 mm are available and only non-destructive techniques preserving sample stratigraphy are allowed to be used. Within this work we show the relation between chemical and mineralogical composition of clay pigments and their provenance. Additionally, the technology of pigment preparation from raw materials can be detected.

We have introduced powder X-ray microdiffraction as modern analytical tool suitable for the direct phase analysis of pigments from 0.1 mm spots on fragments of paintings. The method extends possibilities of traditional tools, optical and electron microscopy (SEM-EDX). X-ray microdiffraction is performed with common X-ray tube and monocapillary producing a quasiparallel beam combined with a sensitive-fast solid-state detector that enable diffractogram acquisition in less than 1 day in spite of so small sample size.

Phase analysis is unique for identification of earthy pigments, very common but diagnostically underestimated artists' materials. Earthy pigments containing clay minerals are of different colours: white, yellow, brown, red, green. We have found that mineral green earths found in paintings as distinct green or bluish green grains, simply called "celadonites", can have variable crystallochemical and phase composition. In some Bohemian wall paintings (Prague, Plasy) these grains are in fact chlorites. In Baroque paintings of A. Kern, celadonites with unusual crystallochemical composition could indicate that the author preferred one, probably unique material from a definite regional source. In earthy green-yellow layers, Fe-smectites are probably more common than it has commonly been expected; we identified green smectites as the main component of traditional Bohemian green earth from Kadan and in currently commercially available "Veronese" green earth.

Fatty red clay applied in Gothic paintings as adhesive ground for gilding ("poliment") was originally called "bole". The term was then extended to all red or yellow earthy grounds of various composition and origin. In fact, not all thin red grounds for gilding contain clays. In fragments of polychrome wooden funeral insignias of Czech kings from tombs in the Prague Castle, pure hematite red was used to give warm colour and the adhesive component should therefore be a protein binder, not clay. In Baroque bole grounds of paintings, direct phase analysis distinguished among materials of typical lateritic composition (kaolinite, hematite, anatase) and other low valuable boles with smectites and illites or, eventually, poorly crystalline goethite and jarosite. Additionally, further signs, revealed by combination of microanalytical methods, indicate that artists calcined or mixed materials of different origin. Because clay minerals are very sensitive indicators of natural processes, they bear unique signs of their regional orgin, and therefore they are extremely valuable for materials research of art works.

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